Contents

Preface ix

1 Introduction 1

2 Humic substances – a brief review 4
  2.1 Natural organic matter and humic substances 4
  2.2 Isolation and classification of humic substances 6
  2.3 Formation and decomposition of humic substances 10
  2.4 Chemical and physical properties of humic substances 13
  2.5 Environmental concentrations of humic substances 24
  2.6 Humic substances – accident or design? 30

3 Environmental solution and surface chemistry 32
  3.1 Solutions and solutes 32
  3.2 Natural particulate matter 34
  3.3 Physico-chemical interactions in environmental aqueous systems 37
  3.4 Equilibrium and kinetics 44
  3.5 Chemical speciation 45
  3.6 Calculation of equilibrium concentrations 46

4 Proton dissociation from weak acids 52
  4.1 Acids and bases 52
  4.2 Buffering 55
  4.3 Kinetics 55
  4.4 Diprotic acids 57
  4.5 Extension to higher polyprotic acids 59
  4.6 Electrostatic interactions among sites 61
  4.7 Proton dissociation from well-defined polymers 73
  4.8 Proton dissociation from humic substances 76
Contents

5 Metal–ligand interactions  77
   5.1 Coordination  77
   5.2 Chemical equilibria involving metal ions, protons and simple weak
      acid ligands  86
   5.3 Multisite ligands  98
   5.4 Electrostatic interactions  99
   5.5 Results with well-defined macromolecules  99

6 Methods for measuring cation binding by humic
   substances  103
   6.1 The humic sample  103
   6.2 Determination of proton binding by potentiometry  104
   6.3 Analytical determination of acid group contents  108
   6.4 Direct measurement of equilibrium metal binding –
      principles  110
   6.5 Separation methods to quantify equilibrium metal binding  113
   6.6 Competition methods  119
   6.7 Electrochemical techniques  121
   6.8 Spectroscopic methods  123
   6.9 Measurement of the kinetics of metal–humic interactions  126

7 Quantitative results with isolated humic substances  128
   7.1 Proton dissociation  128
   7.2 Equilibrium binding of metal ions  136
   7.3 Kinetics of metal ion binding  151

8 Cation binding sites in humic substances  157
   8.1 Proton-dissociating groups  157
   8.2 Binding sites for metals – information from binding studies  159
   8.3 Information from spectroscopy  162
   8.4 Viscometry  169
   8.5 Summary  169

9 Parameterised models of cation–humic interactions  171
   9.1 Overview and philosophy  171
   9.2 Models that describe the binding of a single cation  173
   9.3 Simpler models that include competition  183
   9.4 The site heterogeneity/polyelectrolyte models of Marinsky and
      colleagues  192
   9.5 Modelling electrostatic effects in humic substances  194
   9.6 Humic Ion-Binding Models V and VI  201
   9.7 The NICA and NICCA models  206
   9.8 Summary  209
10 Applications of comprehensive parameterised models 210
10.1 Interactions with protons 210
10.2 Binding of single metal cations interpreted with Model V 216
10.3 Binding of single metal cations interpreted with Model VI 220
10.4 Application of the NICCA model 229
10.5 Metal binding as a function of ionic strength 235
10.6 Non-specific binding 240
10.7 Competition between metals 240
10.8 Proton–metal exchange 246
10.9 Comparison of the NICCA–Donnan model and Model VI 249
10.10 Applications of the models to field situations 251

11 Predictive modelling 253
11.1 Electrostatic interactions 253
11.2 Binding sites 254
11.3 Prospects for predictive modelling 260

12 Cation–humic binding and other physico-chemical processes 262
12.1 The conformation of humic matter 262
12.2 Aggregation of humic substances 266
12.3 Adsorption of humic substances by mineral surfaces 270
12.4 Binding of organic cations by humic substances 278
12.5 Colloid stability 278
12.6 Dissolution of minerals 282
12.7 Formation of mineral precipitates 285
12.8 Other processes 287
12.9 Concluding remarks 287

13 Cation binding by humic substances in natural waters 288
13.1 Chemical speciation calculations 288
13.2 Interactions with major ions and protons 290
13.3 Interactions of humic substances with major cations 301
13.4 Competition 308
13.5 Interactions of heavy metals with humic substances in natural waters 315
13.6 Modelling heavy metal speciation in natural waters 320
13.7 Interactions with metallic radionuclides 331
13.8 Binding by dissolved humic matter compared to adsorption by suspended particulates 331
14 Cation binding by humic substances in soils and sediments 334
14.1 Components of the soil system 335
14.2 Sorption of major cations by organic-rich acid soils 339
14.3 Sorption of major cations by mineral soils 347
14.4 Sorption of trace cations by soil solids 352
14.5 Dissolved organic matter (DOM) in soil solution 359
14.6 Colloids in soil and aquifer porewaters 371
14.7 Cation–humic interactions in sediments 371

15 Research needs 380
15.1 Research needs for isolated humic materials 380
15.2 Research needs in field studies 385
15.3 Cation–humic interactions in catchments 387

References 391
Index 422